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## Flux of nutrients between the middle and southern Adriatic Sea (Gargano-Split section)

Federica Grilli <sup>a,\*</sup>, Mauro Marini <sup>a</sup>, Jeffrey W. Book <sup>b</sup>, Alessandra Campanelli <sup>a</sup>, Elio Paschini <sup>a</sup>, Aniello Russo <sup>a,c</sup>

- <sup>a</sup> Institute of Marine Sciences, National Research Council (CNR), Largo Fiera della Pesca, 2, IT-60125 Ancona, Italy
- <sup>b</sup> Ocean Sciences Branch, Naval Research Laboratory, Stennis Space Center, 39529 MS, USA
- <sup>c</sup> Dipartimento di Scienze della Vita e dell'Ambiente, Università Politecnica delle Marche, Via Brecce Bianche 60131, Ancona, Italy

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#### ABSTRACT

The transect Gargano-Split at the borderline between the middle and southern Adriatic on the Palagruža Sill is exposed to the influences both from the northern and southern Adriatic and is a main transition point for the Adriatic. Thus, water and dissolved inorganic nutrients fluxes between the northern shelf area and the southern deep sea can be estimated at this point. During the Dynamic of the Adriatic in Real Time (DART) project, 12 bottom-mounted Acoustic Doppler Current Profilers (ADCPs) were deployed from November 2005 to September 2006 along the Gargano-Split section. During the same period four different oceanographic cruises were carried out (in November 2005, March, April and July 2006). Hydrographic stations were sampled with the CTD/Rosette to measure physical (temperature, salinity and density) and chemical (oxygen, orthosilicate, orthophosphate and nitrite+nitrate) parameters. Measurements of current velocities allowed estimation of water fluxes and the net nutrient transports were estimated from these and nutrient concentrations. The orthosilicate flux across the transect for inflow and for outflow was higher (except for March) than the nitrite + nitrate and the orthophosphate fluxes. The outflowing nutrient fluxes in the Western Adriatic Current (WAC) were much lower than the total nutrient flux outflow as a large portion of the nutrient flux towards the southern Adriatic was carried by other outflowing waters including North Adriatic Dense Water (NAdDW) flowing along the Italian bottom slope and Middle Adriatic Dense Water (MAdDW) flowing through the deepest passage in the center of the Sill. The July survey provided the first opportunity for direct measurements of total nutrient fluxes across a full basin transect of the central Adriatic. The measurements suggest that the nutrient import and nutrient export were roughly in balance. Modified Levantine Intermediate Water (MLIW) significantly contributed to a total nutrient influx across the transect that was strong enough to counter-balance the nutrient export by the WAC, NAdDW, MAdDW, and other sources.

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#### 1. Introduction

The Adriatic Sea is a small, semi-enclosed shelf sea of the Mediterranean connected to Eastern Mediterranean through Otranto Strait which is 75 km wide and 800 m deep. According to its topography, it is divided into the northern, middle and southern Adriatic. The northernmost part is very shallow (about 50 m) and is highly influenced by the large amount of fresh water coming from the Po River which spreads southward along the Italian coast. The middle Adriatic is deeper reaching a depression of 270 m (Jabuka Pit). The Palagruža Sill (170 m) divides this part from the southern Adriatic where the maximum depth is 1250 m (Cushman-Roisin et al., 2001).

E-mail address: f.grilli@ismar.cnr.it (F. Grilli).

The transect Gargano-Split in the middle Adriatic (close to the borderline between the middle and southern Adriatic) is exposed to the influences from both the northern and southern Adriatic and its dynamics are also influenced by the topographic effect of the Palagruža Sill. This Sill is an area with a strong temporal variability of thermohaline structure caused by seasonally dependent circulation in the surface and intermediate layer (Marini et al., 2006).

Historical hydrographic and moored current meter data indicate that the mean surface circulation of the Adriatic consists of a basin-wide cyclonic gyre with a northward flow along the eastern side (Albanian and Croatian coasts), the Eastern Adriatic Current (EAC; Marini et al., 2010) and a southward return flow along the Italian coast on the western side (Western Adriatic Current; WAC; Zore-Armanda, 1963; Orlić et al., 1992; Artegiani et al., 1997a, 1997b) which flushes the nutrient-rich water out of the northern Adriatic (Hopkins et al., 1999; Marini et al., 2002; Marini et al., 2008). The northwestward flowing water on the eastern side tends to turn cyclonically around the Jabuka Pit in the central

<sup>\*</sup> Corresponding author at: National Research Council (CNR), Institute of Marine Sciences (ISMAR), I.g. Fiera della Pesca, 2, 60125 Ancona, Italy. Tel.: +39 0712078842; fax: +39 07155313.

region and joins the southeastward return flow. During autumn and winter a cold and relatively fresh dense water mass (North Adriatic Dense Water; NAdDW) is formed in the northern Adriatic Sea and from time to time is advected across the Palagruža Sill. Numerous studies (e.g., Zoccolotti and Salustri, 1987; Bignami et al., 1990a; Vilibić and Orlić, 2002; Vilibić and Supić, 2005; Carniel et al., 2012) have observed that during autumn and winter the NAdDW forms a cold bottom density current over the western Adriatic shelf at the depth between 100 and 200 m and arrives at Gargano Peninsula and offshore Bari in the following spring and summer. Outflowing NAdDW is accompanied by inflowing warmer Modified Levantine Intermediate Water (MLIW) from the Mediterranean and this thermal circulation is driven by winter cooling of the Adriatic (Orlić et al., 2006).

The Middle Adriatic Dense Water (MAdDW) forms in the middle Adriatic and resides throughout the year in the bottom layer of the Jabuka pits (Marini et al., 2006). When large quantities of MAdDW are produced, this water can overtop the Jabuka pits, joining with the NAdDW and going towards the southeast. At intermediate depths, the Gargano-Split transect is also under the influence of the advection of saltier water from the southern Adriatic as MLIW is salty as well as warm. MLIW influence is evident as a maximum in the salinity field and reflects the broader Mediterranean influence into the Adriatic Sea. The inflow of this water from the Ionian Sea is also a major supplier of nutrients. Gačić et al. (2010) show that the salinity of the Ionian inflow to the Adriatic undergoes decadal variations according to varying inputs of MLIW and Modified Atlantic Water, and this dynamic should also influence the nutrient input along the Gargano-Split transect.

River runoff affects the circulation through buoyancy input, which is one of the major driving forces of the WAC and impacts the ecosystem by introducing large amounts of organic matter, nutrients, salts, and sediments. The inshore and surface portion of the WAC is a relatively fresh meandering stream carrying low salinity coastal water that is strongly augmented by the Po River outflow. This flow is separated from the circulation in the interior by a more or less sharp (depending upon season) temperature, salinity, and hence density front, roughly paralleling, but frequently expanding seaward of the 40-m isobath. The long-term changes of the nutrient concentrations in the northern Adriatic are connected with climatic fluctuations, which can modify both the hydrological cycles (e.g. the Po flow-rate) and the water dynamics in the sea (vertical mixing, horizontal advection and the water exchange rate between the northern and central Adriatic; Degobbis et al., 2000).

The seasonal discharge of most rivers flowing into the Adriatic Sea has been estimated (Raicich, 1994; Marini et al., 2010), but daily discharge figures are only readily available for the Po River. The mean annual runoff of all these rivers is  $5.7 \times 10^3 \text{ m}^3 \text{ s}^{-1}$ . The Po River, which is the largest, has a mean annual runoff of about 1527 m³ s $^{-1}$  and a spring maximum of 3400 m³ s $^{-1}$  (Raicich, 1994, 1996). The mean observed discharge of the Po from December 2005 through August 2006 was 687 m³ s $^{-1}$  versus 1527 m³ s $^{-1}$  for climatology (Raicich, 1994); hence the Po discharge during the period of this study was significantly lower than its mean value.

Being a continental basin, the Adriatic Sea circulation and water masses are strongly influenced by atmospheric conditions, primarily winds. Using idealized and realistic numerical simulations of the Adriatic, Magaldi et al. (2010) studied and assessed the response of the WAC to wind forcing. They found that the turbulent regimes set up by different winds affect mixing and the WAC transport. With downwelling winds, the transport is generally southward and mixing happens mostly between the fresher ( $S \le 38$ ) salinity classes. With upwelling winds, the transport decreases and changes sign, and mixing mainly involves saltier (S > 38) waters. In summer, near Cape Gargano, mesoscale eddies and filaments have been observed to exhibit horizontal and vertical scales of about 30 km and 25 m, respectively, and a quasi-permanent anti-cyclonic circulation is often observed downstream of the cape (Burrage et al., 2009).

In summer, winds are usually relatively weak, but such conditions can be interrupted by short periods of strong winds from the northeast (Bora) or southeast (Sirocco). Bora events, which occur more frequently in winter (Cushman-Roisin et al., 2001), seem to be able to generate a relevant increase of nutrient export from the northern Adriatic through intensification of the WAC, so they could play a relevant role in the nutrient balance of the basin (Boldrin et al., 2009). During Bora events, sediments with nutrients and other waterborne material are resuspended and driven southward along the Italian coast (Lee et al., 2005; Marini et al., 2008).

The Eastern Mediterranean is ultra-oligotrophic area with high nitrate to phosphate ratio in deep waters, about 28:1 (Krom et al., 1991, 2004, 2010). As a consequence, the typical winter phytoplankton bloom is P rather than N limited. The only exception is the northern Adriatic where high primary production and eutrophication are caused by high river nutrient loads (Degobbis et al., 2000). However horizontal or vertical advection and displacement of nutrients in the Adriatic may cause shifts in primary production at specific locations such as the South Adriatic where phytoplankton blooms follow deep convection events (Vilibić and Šantić, 2008). Vilibić et al. (2012) investigating a long-term time series of physical and chemical parameters along the Palagruža Sill transect between 1960 and 2010, found that the primary production was controlled by nitrogen availability between 1991 and 1998 in the euphotic zone indicating a switch from typical phosphorous to nitrogen-limited conditions.

Most previous chemical fluxes for the Adriatic have been estimated for either the northern (Degobbis and Gilmartin, 1990; Grilli et al., 2005) Adriatic or the Strait of Otranto (Civitarese et al., 1998) in the southern Adriatic. However, the transition point between a continental shelf and a deep basin occurs in the middle Adriatic Sea and very few studies have been carried out about the flux of nutrients there. Moreover, the distribution of biogeochemical properties in the middle Adriatic is scarcely documented and the net transport of material off the shelf between the northern and southern Adriatic is poorly known

Gačić et al. (1999) used hydrographic and current measurements to estimate southward water and biogeochemical fluxes along a section from the 50 m isobath near the Italian coast southeast of the Palagruža Sill out to the Croatian territorial water limit encountered 90 km offshore on their section. By comparing the results from this section to others in the northern and southern Adriatic, they found that the northern Adriatic adds only 3–4% of the total water volume exchanged through the Strait of Otranto. They concluded that overall the Adriatic acts as a mineralization region despite the productivity of the northern shelf.

The purpose of this work is to add to these limited results by presenting the distribution and flux of nutrients across the transect Gargano-Split, directly on the Palagruža Sill, obtained from measurements of moored current velocities collected data from 2005 to 2006 and seasonal samplings of chemical parameters collected during four oceanographic cruises (November 2005, and March, April, and July 2006). These new estimates not only provide a different year realization from Gačić et al. (1999), but also the July section provides the first full cross-basin measurement of nutrient flux for the middle Adriatic. We also focus on characterizing water and nutrient fluxes according to individual water masses, NAdDW, MAdDW and MLIW, based on the definitions of Vilibić and Orlić (2002).

#### 2. Methods

#### 2.1. Seawater collection

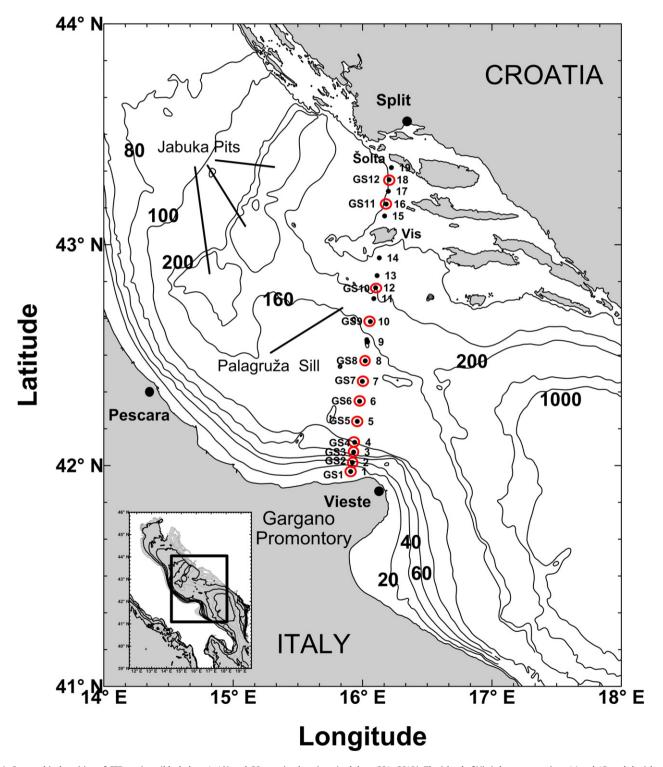
The collection of seawater samples and CTD casts were made on four oceanographic surveys (Table 1a; 08 November 2005, 26 March 2006, 24 April 2006, and 18 July 2006). The cruises were performed on board the Italian R/V Dallaporta. The spatial distribution of the sampling locations is given in Fig. 1. Only the cruise made in July

**Table 1a**List of the cruise dates carried out for the section Gargano-Split with the number of CTD casts and ADCPs.

Date	Research vessel	Casts	ADCPs
08 November 2005	G. Dallaporta	9	12
26 March 2006	G. Dallaporta	9	12
24 April 2006	G. Dallaporta	11	12
18 July 2006	Alliance	19	11
08 November 2005 26 March 2006 24 April 2006	G. Dallaporta G. Dallaporta G. Dallaporta	9 9 11	12 12 12

crossed the basin, the others are up to the Croatian territorial water limit.

Seawater samples were collected with Niskin bottles mounted on a rosette at 2–8 oceanographic depths (surface, 10, 30, 50, 100, 130, 150 and 2 m above the bottom), depending on station bottom depths (Table 1b). The samples were filtered (HA Millipore, 0.45 Am) and stored at  $-22\,^{\circ}\mathrm{C}$  in polyethylene vials and analyzed within two months after returning to port. Nutrient concentrations (ammonium—NH<sub>4</sub>, nitrite—



**Fig. 1.** Geographical position of CTD stations (black dots, 1–19) and GS mooring locations (red dots, GS1–GS12). The Island of Vis is between stations 14 and 15, and the Island of Šolta is located just north of station 19. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Table 1b** ADCPs depth, location and water sampling depths.

Station name	Water column depth (m)	Distance from GS1 (km)	Water sampling depths (m)
GS1	17	0	s,10,b
GS2	33	4.7	s,10,b
GS3	86	9.9	s,10,30,50,b
GS4	100	14.9	s,10,30,50,b
GS5	116	25.8	s,10,30,50,b
GS6	129	35.5	s,10,30,50,b
GS7	126	46.2	s,10,30,50,100,b
GS8	131	56.5	s,10,30,50,100,b
GS9	172	81	s,10,30,50,100,150,b
GS10	146	99.2	s,10,30,50,100,b
GS11	92	134.9	s,10,30,50,b
GS12	99	151.2	s,10,30,50,b

s-surface; b-bottom

NO<sub>2</sub>, nitrate—NO<sub>3</sub>, orthophosphate—PO<sub>4</sub> and orthosilicate—SiO<sub>4</sub>,) were measured using a Bran + Luebbe QUAATRO autoanalyzer. The elaboration of the data analyses was carried out with an appropriate software (AACE®) supplied by Bran + Luebbe. Nutrient analyses utilized modifications of the procedures developed by Strickland and Parsons (1972).

Determination of ammonium utilizes the Berthelot reaction, in which a blue-green colored complex is formed which is measured at 660 nm. A complexing agent is used to virtually eliminate the precipitation of calcium and magnesium hydroxides. Sodium nitroprusside is used to enhance the sensitivity of this method.

Nitrite is measured by reacting the sample under acidic conditions with sulfanilamide to form a diazo compound that then couples with N-(1-Naphthyl)-ethilenediamine to form a reddishpurpleazo dye that is measured at 550 nm. Nitrate is first reduced to nitrite at pH 8 in a copper-cadmium redactor then reacted in the same way as nitrite. Nitrate is corrected for nitrite contribution by correcting for the efficiency of nitrate reduction and subtracting the nitrite concentration measured in an unreduced portion of the sample.

Orthophosphate determination is a colorimetric method in which a blue compound is formed by the reaction of phosphate, molybdate and antimony followed by reduction with ascorbic acid. The reduced blue phosphor-molybdenum complex is read at 880 nm.

The procedure for the determination of soluble orthosilicates is based on the reduction of a silico molybdate in acid solution to molybdenum blue by ascorbic acid. Oxalic acid is introduced to the sample to minimize interferences from phosphate. The absorbance is measured at 660 nm.

Dissolved inorganic nitrogen (DIN) was calculated as the sum of the  $NH_4$ ,  $NO_2$  and  $NO_3$  concentrations.

#### 2.2. Current field

Bottom-mounted, upward-looking Acoustic Doppler Current Profilers (ADCPs) were deployed in October 2005 by the U.S. Naval Research Laboratory (NRL) during the Dynamic of the Adriatic in Real Time (DART) experiment together with the NATO Undersea Research Centre (NURC). ADCPs were recovered in September 2006, so they collected 11 months of data. DART moorings consisted of 12 ADCPs (Table 1b) in trawl-resistant housings called BARNY (due to their barnacle like shape, see Perkins et al., 2000), deployed along a line crossing the Palagruža Sill from the Gargano Promontory, Italy toward Split, Croatia (GS1–12, Fig. 1).

ADCP settings and configurations varied across the 12 sites due to the varying bottom depths and necessary tradeoffs between measurement range, resolution, and accuracy. Depth cells varied between 0.5 m resolution at the shallowest sites to 5 m resolution at the deeper sites, and measurements were generally made using ensembles of 44–114 second (depending on site) bursts of 1 Hz acoustic pings taken every 15 min. As standard, due to ADCP ringing and surface side-lobe contamination,

measurements were not taken or were discarded in zones very near the ADCP transducer head (bottom of the water column) and near the sea surface. The latter combined with some of the deeper ADCPs being deployed at near their maximum range led to a 2 to 15 m (depending on site) depth limit below the sea surface before accurate velocities were obtained. Site GS9, at 173 m depth, was deployed significantly deeper than the others and measurements were not often accurate any closer than 45 m from the surface for this one site. Despite mooring recovery, refurbishment, and redeployment midway through the experiment to counter corrosion development, GS11 failed on 22 June and GS9 on 30 July, 2006. All the other mooring durations spanned a 10–11 month time period. Further details of the DART ADCP settings, deployments, and measurement accuracies can be found in Martin et al. (2009).

Before use in this paper, ADCP data were filtered with a 2-hour low-pass filter (to reduce noise), reduced to hourly values, and interpolated to uniform 0.5 m depth levels. Then the data were detided at each depth level using a tidal harmonic analysis solution for the 7 major constituents of the Adriatic Sea  $(O_1, P_1, K_1, N_2, M_2, S_2, K_2)$ , and finally a further 48-low pass filter was applied to reduce non-tidal higher frequency variability which can alias nutrient fluxes especially due to the possibility of significant transport fluctuations from Adriatic seiches with periods of 22 h. The component of the current perpendicular to the section (oriented 9.5° clockwise from True North) was used for transport computations. The filtered current field was then averaged over the day of the hydrographic section, interpolated using a kriging methodology over a regular horizontal grid and the flux of the water across the transect was calculated.

#### 2.3. Fluxes estimation

Calculating fluxes and transports from point samples distributed along a section require assumptions to be made concerning boundary conditions along the edges of the sections. In the portion of the transport section adjacent to a coast, it is important to know what fraction of this zone is occupied by the lateral frictional boundary layer and therefore what form of extrapolation will best represent the velocity structure between the coast and the location of the nearest velocity measurement. In particular, our section has four different horizontal boundaries as the island of Vis (Fig. 1) adds two boundaries in addition to the section edges at the Italian coast and the Croatian island of Šolta. Using a horizontal eddy diffusivity,  $A_h$ , of 100 m<sup>2</sup> s<sup>-1</sup> (Hendershott and Rizzoli, 1976), the associated planetary boundary layer thickness,  $\sqrt{2A_h/f}$ , for the section boundaries is 1.4 km and the "deep ocean" Reynolds number (Tomczak, 1988), uL/A<sub>h</sub>, for flow around Vis is 14.6. In these calculations, *f* is the Coriolis parameter, u is a characteristic velocity (0.2 m s<sup>-1</sup>), and L is a characteristic length scale (the width of the island of 7.3 km). This indicates that the flow around Vis is likely weakly turbulent and that GS1, GS10, GS11, and GS12 at distances of 4.8, 18.0, 10.4, and 7.3 km from the coast are all far outside the boundary layers. Based on these results we used a free-slip boundary condition for all 4 horizontal section boundaries.

However, to test the sensitivity of this choice we also recalculated the section transports using a no-slip boundary condition for all four boundaries, which acts to reduce the transport values due to the imposition of larger lateral friction zones. Comparing the case of no-slip at every boundary versus free-slip at every boundary for all four surveys, we estimate possible bias errors in transport due to horizontal boundary condition assumptions as 0.02 Sv outflow and 0.14 Sv inflow. The larger potential bias for inflow is due to the fact that generally three lateral boundaries are in the inflowing current zone and the only lateral boundary generally in the outflowing current zone is the smallest in depth of the four boundaries.

For the bottom and top boundaries, the kriging method is used to extrapolate to the surface and to the bottom (defined by the mooring

and CTD bottom depths) with the exception of mooring GS9. This mooring typically had a 45 m surface data gap as previously explained and thus did not contain any measurements from the surface mixed layer zone unlike the other moorings which captured the lower portion of this layer. Therefore at GS9 geostrophic shears calculated from the hydrographic measurements referenced to the ADCP velocity at 60 m were used to extrapolate to the surface rather than using kriging to extrapolate.

The nutrient concentrations, expressed in  $\mu$ mol L<sup>-1</sup>, were interpolated to the same regular grid as the velocities (grid spacing 1 km  $\times$  1 m). The nutrient fluxes were computed by multiplying nutrient concentration by velocities converted to  $m s^{-1}$  and integrating the result over the cross-sectional area. The WAC transport was computed between the coast and a variable position along the transect according to the current (>15 cm s<sup>-1</sup>) and thermohaline fields (Nov. temp. > 18  $^{\circ}$ C and salt. < 38.6; Mar. temp. < 12.5 °C and salt < 38.5; Apr. temp. > 13.5 °C and salt. < 38.3; Jul. temp. > 23.5 °C and salt. < 38.3). This offshore location used to terminate the transport calculation varied between GS4 and GS6 (Fig. 1). On the basis of the water mass characteristics given by Vilibić and Orlić (2002) nutrients fluxes carried by individual water masses were estimated: NAdDW (temp. 9.8–11.4 °C, salt, 38.02–38.58), MAdDW (temp. 10.87–12.37, salt. 38.32–38.62), and MLIW (temp. 13.7-14.3, salt. 38.60-38.90). Nutrient concentrations were used to discriminate between MAdDW and NAdDW when water mass thermohaline properties fell into both ranges (MAdDW is characterized by high nitrate concentrations, nitrite + nitrate > 3  $\mu$ mol L<sup>-1</sup>, with respect to NAdDW; Marini et al., 2006).

#### 3. Results

#### 3.1. Velocity field and water transport

The velocity field (Fig. 2) was highly complex and variable, with mainly an inflow on the northern (Croatian) side and an outflow on the southern (Italian) side, and a more complex and variable structure in the central part. However, at GS9 an outflowing bottom current was present in the deepest part of the sill during three out of the four surveys, transporting bottom cold waters (described in the next section) to the southern Adriatic. The WAC as a concentrated core of outflowing current over the Italian slope was present in all four surveys, but the EAC had a more varying structure and no consistent form from survey to survey.

Of the four surveys, November was the only one that had a flow pattern matching the standard picture of outflow all on the southwestern coast and inflow all on the northeastern coast of the Adriatic. Inflow and outflow occupied the entire water column except at the point of flow reversal which occurred near the GS section midline. The WAC had a vertically sheared core structure centered on GS3 with a velocity maximum of more than 25 cm s<sup>-1</sup>. The EAC in November also seemed to have a vertically sheared core structure with velocity maxima of more than 20 cm s<sup>-1</sup> at both GS10 and GS11 on either side of the island of Vis. The outflow transport in November was the largest of the four surveys (Table 2).

In March the WAC was closer to the Italian coast with a shallow core centered on GS2 and weaker surface flows extending out to GS5–6., However, along the Italian slope, particularly at depths between 110 and 130 m, there was a depth intensified bottom current reaching outflow speeds of 15 cm s<sup>-1</sup>. This outflow corresponded to a core of cold and dense water along the slope (Fig. 3) and therefore it can be said that the signal of outflowing NAdDW was clearly present in the residual current field for March 2006. The EAC in March was relatively strong and concentrated near GS10, but with weaker flows in the channel between Vis and Šolta.

During March, strong inflow was observed at GS7 with outflow observed to either side at GS6 and GS8. This inflow was connected with a core of higher temperature and salinity (Figs. 3 and 4) waters

producing a signature of a warm-core anticyclonic eddy centered between GS7 and GS8. This submesoscale feature is somewhat long lived as it appears in 48 hour filtered data and may be undergoing interaction with the EAC as the outflow side near GS8 appears to be weaker than the inflow side at GS7. An alternate possible explanation is that this feature could be a strong inflowing filament of warm water that has separated from the EAC core upstream of the section.

The current field in April showed a variable structure that alternated between outflow and inflow. The WAC was concentrated near the Italian coast with its core centered at GS3, but the inflow was distributed in various alternating bands all the way from GS4 to GS12 and a clear EAC core cannot be distinguished (e.g., GS10 is characterized mostly be outflow in April). Bottom currents were still intense along the Italian slope, concentrated in the same areas as in March where cold, dense waters were still present (Fig. 3). Thus outflow of NAdDW continued to occur in 2006 through April.

The current field in July was similar to that found in March, except that bottom currents were now much weaker, and the WAC was mainly evident in the surface layer above the now strongly formed thermocline (Fig. 3). The bottom water along the Italian slope was warmer than in March and April indicating that the outflow of NAdDW had mostly stopped by July in 2006.

Maximum outflow velocities for the WAC were found in July reaching 25–30 cm s<sup>-1</sup> in its 20 m deep core at GS3. However, the overall outflow was weaker than in any other survey (Table 2). The EAC lacked the concentrated structure seen in November and March, producing less inflow than those two surveys but more than in the April survey. The mooring at GS11 failed before this survey so the flow between Vis and Solta was not very well resolved leading to potentially larger errors especially regarding the inflow transport calculations than for other surveys. A sensitivity analysis was conducted by computing volume transports for the entire period when all 12 GS moorings were deployed and then recomputing volume transports for the same period with GS11 data removed. This analysis indicates that inflow could potentially be too low by 0.04  $\pm$  0.12 Sv and outflow could potentially be too high by 0.01  $\pm$  0.05 Sv when GS11 data are absent from the calculation. If this analysis is restricted to the last month (April 23-June 22) before GS11 failure, the potential biases increase in magnitude but the variances decrease suggesting that inflow could be too low for the July survey by  $0.07 \pm 0.06$  Sv and outflow could be too high by  $0.03 \pm 0.03$  Sv due to the failure of GS11.

Our inflow and outflow transport calculations (Table 2) do not exactly agree with each other for any survey, but boundary assumption errors (see Section 2.3) and the failure of GS11 for July could account for a large portion of these differences. Furthermore, imbalances of these orders are possible for the Adriatic even over monthly time periods (0.05 Sv over one month produces a sea-level change of the northern half of the Adriatic of about 1 cm). To further examine this question, we used the results of the sensitivity test for volume transport when all 12 GS moorings were functional and extended the test to also include transport calculations for late June through July when GS11 had failed. Overall in this test, inflow was higher than outflow by an average of 0.11 Sv and the std of the difference time series between inflow and outflow was 0.25 Sv. Therefore even the largest inflow/outflow difference from the surveys of 0.27 Sv in July is not outside the expected norms compared to other times. As the outflow was generally concentrated in the WAC and better resolved by the mooring distribution, errors are expected to be lower than for the inflow and the outflow should better represent the true transport through the section. I.e., much of the 0.11 Sv greater average transport found for the inflow is likely an artifact of lower mooring resolution from GS8 to Solta compared to the resolution from Italy to GS8 (Table 1b).

The Po river runoff affected the circulation through buoyancy input and contributed to the WAC flowing towards the southeast along the Italian coast. The WAC was present in all the surveys and

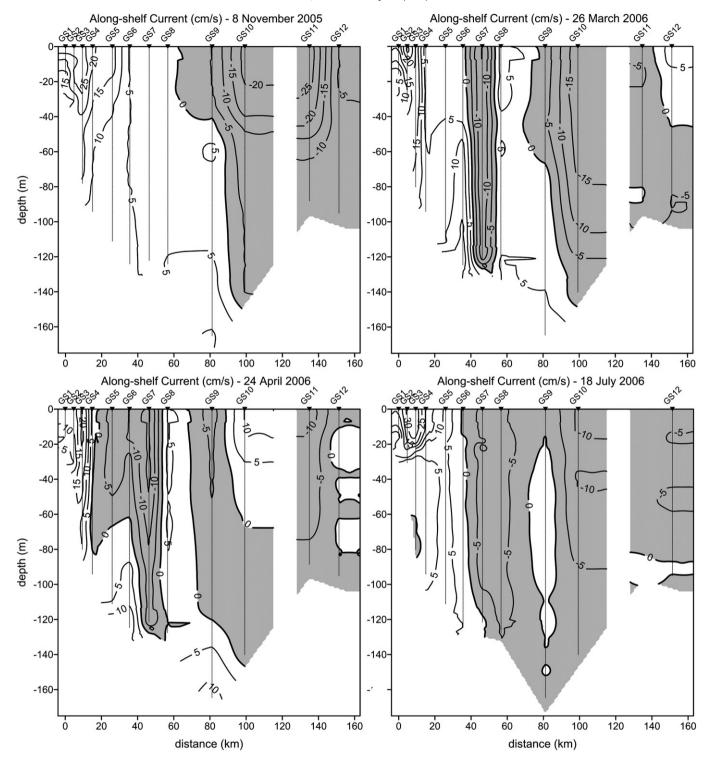


Fig. 2. Current field (cm s<sup>-1</sup>) across the section Gargano-Split; positive values indicate along-shelf east component (outflow) while negative values indicate inflowing west component.

**Table 2**Estimated water fluxes values (Sv) along the section during the four oceanographic surveys.

November 2005		March 20	06	April 2000	6	July 2006	
Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow
0.68	0.78	0.55	0.70	0.38	0.42	0.27	0.54

is known to possibly be a concentrated area of nutrient export to the south, so we computed water and nutrient transports specific to that current (Table 3). The water flux estimate in the WAC varied from a low of 0.07 Sv in April to a high of 0.21 Sv in November. These estimates are in agreement with the transports observed along the Italian slope (mean of 0.15 Sv) in the Northern Adriatic in 2002/2003 (Book et al., 2007). However, it is clear that the WAC defined in this way is

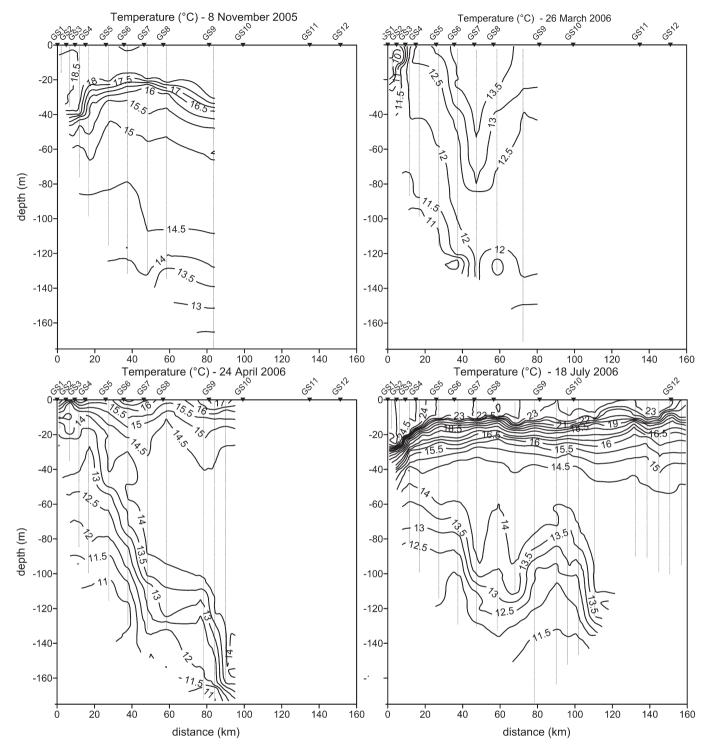


Fig. 3. Vertical sections for temperature (in °C) during the four different surveys.

carrying less than 60% of the total outflow across the sill to the Southern Adriatic for all four surveys, and it is carrying less than 20% of the total outflow for the March and April surveys (Tables 2 and 3).

#### 3.2. Thermohaline fields and nutrient concentrations

Temperature fields (Fig. 3) showed structures typical of the seasonal cycle of the Adriatic. In November the thermocline was quite weak and relatively deep, as typical in autumn, in March it was almost absent as typical in winter, in April it was forming with an

evident surface warming as typical in spring, and in July it was quite shallow and strong as typical in summer, with changes of up to 8 °C in less than 20 m. In all the periods, the temperature at the deepest part of the sill (GS9) was below 13 °C, with a minimum below 11 °C in April, and a maximum near 12.5 °C in November, when almost no trace of NAdDW was evident there and the deepest part of the section was occupied by MAdDW.

The lowest temperature values were recorded in March near the Italian coast, reaching a minimum value below 10 °C in the upper layer associated with freshwaters. Cold waters with temperature

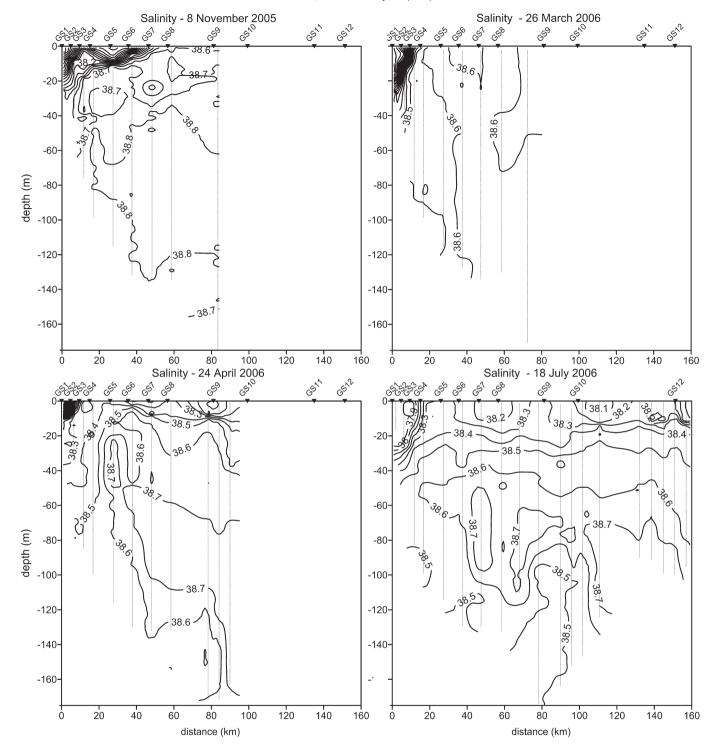


Fig. 4. Vertical sections for salinity during the four different surveys.

below 12 °C (NAdDW) occupied the western bottom slope, reaching values below 11 °C in a thin layer between GS4 and GS7. The deepest part of the section was occupied by MAdDW, which is slightly warmer

**Table 3**Water fluxes (Sv) estimated in the WAC along the section during the four oceanographic surveys.

Transport in the Western Adriatic Coastal Current ( $10^6 \text{ m}^3 \text{ s}^{-1}$ )							
November 2005	March 2006	April 2006	July 2006				
0.21	0.10	0.07	0.15				

and saltier than NAdDW, and is further revealed by its high nitrogen content as discussed in Section 2.3. In April, NAdDW was still abundant on the slope, but the presence of MAdDW was diminished. In July the whole layer below 90–100 m depth was occupied by a dense, cold water mass likely derived from the past winter's NAdDW which was dense enough to reach the bottom of the Jabuka Pits and renew MAdDW. In November and March MAdDW was outflowing as a compact core into the southern Adriatic through the deepest passage in the center of the Sill. In April, this deep passage was also outflowing into the southern Adriatic carrying both NAdDW and MAdDW, but in July this flow was nearly stagnant (Fig. 2).

The salinity distribution (Fig. 4) showed a surface minimum (<38) close to Italian coast in all the surveys, heavily influenced by the freshwater discharge coming from the northern basin. Its width, however, varied in time reaching a minimum in March when it did not exceed 10 km, due to the smaller horizontal length scales in this period (late winter). In November, April and July, the signal of MLIW (salt. > 38.6 with temp. between 13 and 15 °C) was evident at intermediate depths; low values of dissolved oxygen (not shown) indicated that this water had had no contact with the surface for a long time (another characteristic of MLIW). In March MLIW was substantially absent in the investigated part of the section.

The nutrient concentrations (Figs. 5, 6 and 7) were highly variable during all the survey periods. November was characterized by low nitrite + nitrate (Fig. 5) values in the surface layer and down through the base of the thermocline (0–60 m) with values ranging between 0.5 and 1  $\mu$ mol  $L^{-1}$ . Higher values (between 2 and 3.5  $\mu$ mol  $L^{-1}$ ) occurred in the bottom layer; this situation could be due to the uptake by phytoplankton groups as evidenced by higher fluorescence values (not shown). On the contrary in March the nitrite + nitrate concentrations had the highest values of the four surveys, both in the surface and in the deep layers. In the surface layer the high values were linked to the lowest observed fluorescence values; this suggests that

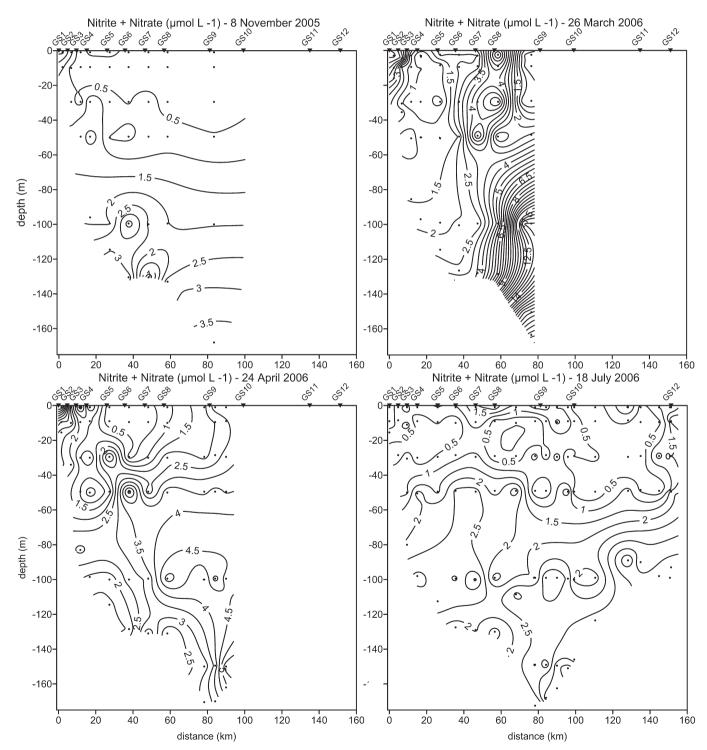


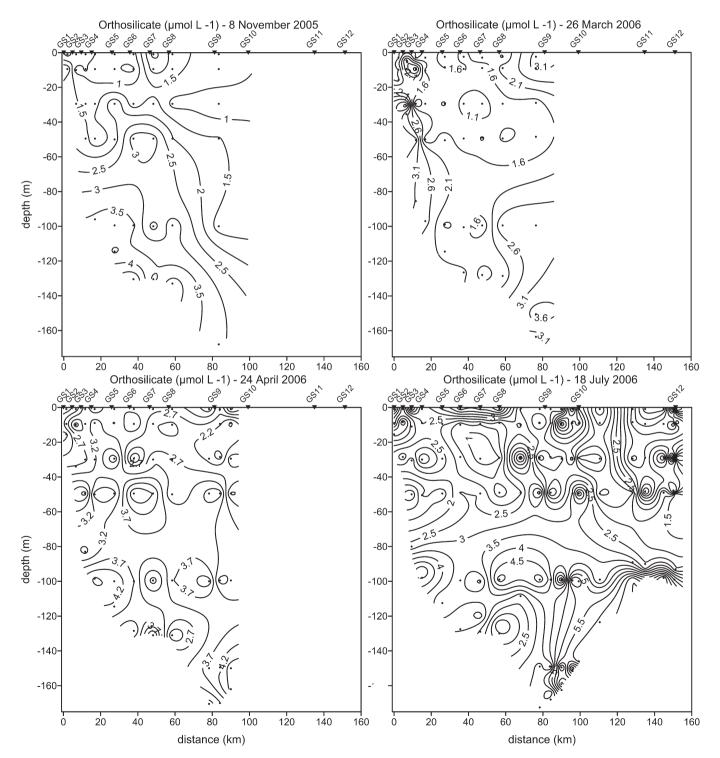
Fig. 5. Nitrite + nitrate sections (in  $\mu$ mol  $L^{-1}$ ) during the four different surveys.

high nutrient concentrations there could be due to a lack of consumption of nutrients by the phytoplankton community. The maximum concentrations (>10  $\mu mol~L^{-1}$ ) over all the surveys were observed in March at the deepest part of the section, revealing old MAdDW overflowing from the Jabuka Pit.

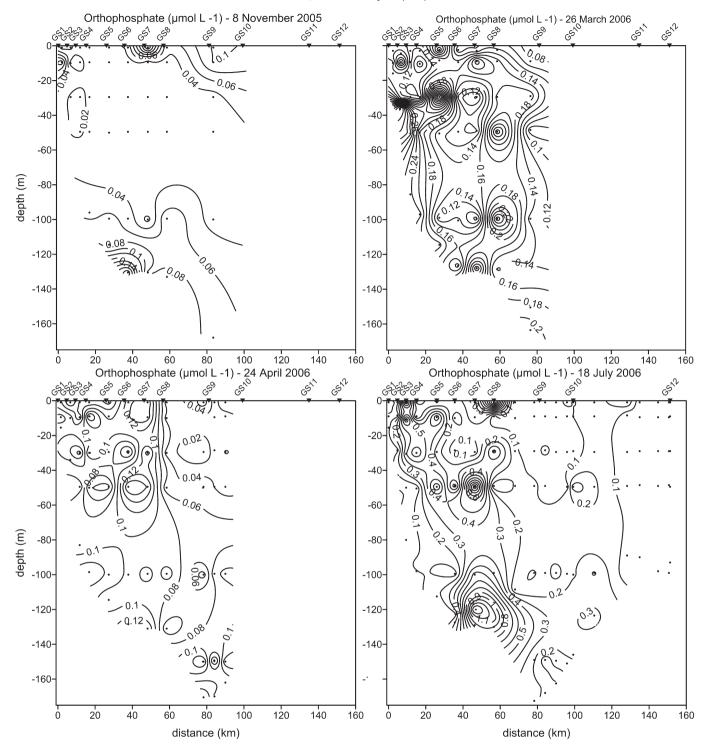
In April and July the nitrite + nitrate distributions were quite similar to those observed in November with generally high concentrations, especially in the bottom layer probably due to processes of remineralization of organic matter and in the intermediate layer due to the advection of older and richer in nutrient water (MLIW)

as revealed also by low oxygen saturation values (not shown, more details are reported in Marini et al, 2006). In July, as in November, the surface layer had low nitrite + nitrate values down to the base of the thermocline, but in July the thermocline was at a shallower depth than in November.

The orthosilicate distribution (Fig. 6) was similar to the nitrite + nitrate with values higher (2–4  $\mu$ mol L $^{-1}$ ) below 50–60 m. The highest values (around 5  $\mu$ mol L $^{-1}$ ) were reached in July in correspondence with MLIW. The distribution of orthophosphates (Fig. 7) showed low values and this can be considered a characteristic of the



**Fig. 6.** Orthosilicate sections (in  $\mu$ mol L<sup>-1</sup>) during the four different surveys.



**Fig. 7.** Orthophosphate sections (in  $\mu$ mol L<sup>-1</sup>) during the four different surveys.

**Table 4** Nutrient fluxes (nitrite + nitrate, orthosilicate and orthophosphate) computed across the transect (units in mol  $s^{-1}$ ).

Nutrients	November 20	05	March 2006		April 2006		July 2006	
	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow
Nitrite + nitrate	974	97	2361	479	784	578	358	748
Orthosilicate	1484	188	1197	249	972	847	702	1403
Orthophosphate	29	10	95	21	25	26	75	120

**Table 5** Nutrient fluxes (mol  $s^{-1}$ ) estimated in the Western Adriatic Current.

	November 2005	March 2006	April 2006	July 2006
Nitrite + nitrate	128	322	152	101
Orthosilicate	249	193	183	337
Orthophosphate	7	15	5	46

Adriatic and the Mediterranean Seas where the phosphorus is often a limiting factor (Campanelli et al., 2011; Zavatarelli et al., 1998).

One of the most noteworthy features was that nitrite + nitrate and orthosilicate were often abundant where orthophosphate was completely depleted, as in November when its concentration was close to the detection limit (0.02  $\mu$ mol L<sup>-1</sup>) across all stations at mid-depth. But the reverse situation also occurred, as in July when in the surface layer the nitrite + nitrate concentration (around 0.5  $\mu$ mol L<sup>-1</sup>) were at a very low level in terms of Redfield ratio when compared to the orthophosphate concentration (0.1–0.2  $\mu$ mol L<sup>-1</sup>).

#### 3.3. Nutrient fluxes

The nutrient transports were estimated from the water fluxes combined with nutrient concentrations for all the cruises. The observed nutrient net fluxes (Table 4) were mainly outflowing from the central Adriatic except in July where the inflow of nutrients was dominating. This is because in July the nutrient measurements were available for the entire transect, so the inflow is dominated by incoming MLIW (which is high in nutrients but not fully captured in the other surveys because the eastern part of the transect was not sampled).

The orthosilicate flux across the transect for inflow and for outflow was higher (except for March) than the nitrite + nitrate and the orthophosphate fluxes, in agreement with the findings of Gačić et al. (1999). The orthosilicate flux calculated in the WAC (Table 5) was also predominant and very high in all the surveys (except for March).

According to the water mass analysis described in Section 2.3, we computed the nutrient fluxes associated with three different water masses, MLIW, NAdDW and MAdDW (Table 6); MLIW fluxes were considered only in July because this water mass is abundant in the eastern part of the Gargano-Split section and any estimate of MLIW nutrient fluxes during surveys when this part of the transect was not sampled would not be accurate. The orthosilicate flux was always the most abundant, except for MAdDW which was distinctly higher in nitrite + nitrate concentrations. In July the bottom water in the deepest part of the sill was classified as NAdDW rather than MAdDW on the basis of low nitrite + nitrate values. It was recently derived from NAdDW sources and had probably not resided in the Jabuka Pit for a long enough time for remineralization to have changed the nutrient content of the waters significantly.

#### 4. Discussion

The calculated values of the water fluxes revealed stronger transports occurring during November and March than during April and July. This is in general agreement with the known seasonal cycle of Adriatic flows (Poulain, 2001). However, it should be noted that

transports in this study period could potentially be altered from typical climatological values due to strongly reduced river runoff. The mean observed discharge of the Po River from September 2005 through August 2006 was 687 m $^3$  s $^{-1}$  versus 1527 m $^3$  s $^{-1}$  for climatology (Raicich, 1994); hence the Po discharge was significantly lower than its mean value (Fig. 8).

According to Gačić et al. (1999), estimates of the southward water and nutrients fluxes indicates that the northern Adriatic adds to the southern Adriatic only 3–4% of the total water volume exchanged through the Strait of Otranto. Grilli et al., 2005 estimated southward nutrient transports in the northern Adriatic Sea from June 1999 to June 2002 across Cesenatico-Cape Kamenjak and Senigallia-Susak Island, finding average values around 1.5 mol s<sup>-1</sup>, 80 mol s<sup>-1</sup> and 60 mol s<sup>-1</sup> for orthophosphate, orthosilicate and dissolved inorganic nitrogen (DIN) respectively. Moreover Boldrin et al. (2009) estimated a southeastward net flux along Cesenatico-Pula transect (northern Adriatic) of 0.11 Sv for water, 8.21 mol s<sup>-1</sup> for orthophosphate, 750 mol s<sup>-1</sup> for orthosilicate, and 355 mol s<sup>-1</sup> for DIN. Considering all these facts, the northern Adriatic, even though being recognized as one of the most productive areas of the Mediterranean Sea, seems not to be exerting an important biological influence on the whole Adriatic.

In fact the water and nutrient fluxes computed across Gargano-Split transect in this study were higher than those obtained in these past studies of the northern Adriatic. This can in part be explained by water rich in nutrients coming from the Jabuka pits where it had been residing for at least 1 year (Marini et al., 2006). These authors showed that the old bottom water was richer in nutrients because of a mineralization processes happening during the resident time inside the pits. Furthermore we find that the WAC itself only comprises less than 60% of the total outflow across the Gargano-Split transect, so already at this location water masses originating from locations other than the northern Adriatic are playing significant roles in the outflow of nutrients to the south. Some portion of the outflow here could also simply be a recirculation of South Adriatic waters and nutrients that temporarily passed over the sill only to return back to the south a short time later.

The nutrient outflow calculated in July (except for orthophosphate) was lower in respect to the ones estimated in other periods, due to the weaker freshwater discharge typical of summer periods, to the weaker circulation regime typical in summer, and to a likely phytoplankton uptake. However, only the July survey had nutrient sampling that spanned the entire section so this is the only survey to date that can be used to directly compare total inflowing and outflowing nutrient fluxes between the central and southern Adriatic. Inaccuracies in the transport calculation were likely the cause of much of the higher inflow volume transport estimate than outflow estimate for this survey. The percentage of outflow to inflow was 50% for water volume, 48% for nitrite + nitrate, 50% for orthosilicate and 63% for orthophosphate. But if we consider that the inflowing water volume is likely overestimated by 20% (0.11 Sv average bias) and that the rest of the inflow/outflow difference is within the typical expected variance over time of this quantity (0.25 Sv std), then we cannot conclude that any of the calculated July net inflows in Table 4 are necessarily sustained imports of nutrients. Accounting for this, we find that the Gargano-Split section was roughly in balance between nutrient import and nutrient export for July 2006 based on

**Table 6** Nutrient fluxes (mol  $s^{-1}$ ) estimated in MAdDW, NAdDW and MLIW.

Nutrients	November 2005		March 2006		April 2006		July 2006	
	MAdDW	NAdDW	MAdDW	NAdDW	MAdDW	NAdDW	NAdDW	MLIW
Nitrite + nitrate	246	243	672	346	203	112	150	- 395
Orthosilicate	271	396	128	419	217	219	203	-590
Orthophosphate	6	7	8	33	5	6	15	-57

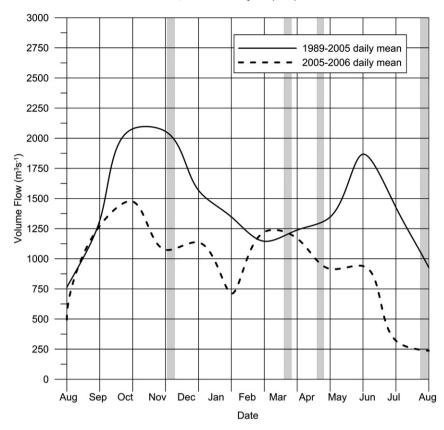


Fig. 8. Daily means of the Po River flow for the period 1989–2005 (solid line) and for the period from August, 1 2005 to July, 31 2006 (dashed line). The columns are the four cruises periods.

the nearly identical percentage differences between nutrient inflow/outflow fluxes and the percentage difference between volume inflow/outflow flux. I.e., the larger nutrient inflows for July in Table 4 are close enough to the outflow values to be indistinguishable from a state of zero net flux balance given the uncertainties of the estimates. Only the flux of Orthophosphate has an outflow to inflow ratio much different than 50%, suggesting that in July there may be some portion of Orthophosphate nutrient export taking place. Taken as a whole, our findings show that at least for July 2006, the northern and central Adriatic are not acting as a significant source of nutrient export to the south, as the nutrients exported by the WAC (Table 5), by NAdDW (Table 6), and by other outflowing waters are more than replaced by an import of nutrients by MLIW (Table 6) and by other inflowing waters.

In interpreting these results one should bear in mind that they were obtained on the basis of a single year realization (2005/06) and the finding of net nutrient flux balance was only based on a single survey, yet it is well know that the year-to-year variations of the oceanographic conditions in the Adriatic are rather large (Gačić et al., 1997). For the first time it has been possible to estimate the nutrient fluxes in the different water masses across the transect separating the northern-central Adriatic shelf area from the deeper southern Adriatic Sea. The nutrient fluxes in the WAC were much lower with respect to the total outflow computed across the transect, and a major part of the nutrient flux toward the southern Adriatic was due to NAdDW and MAdDW. MLIW, at least in July, carried a nutrient flux into the northern Adriatic shelf area equal or greater to the export of nutrients out of the shelf from these three other sources. All of these results are probably influenced by the very low Po River runoff during the sampling period, so further investigation in different conditions is needed in order to confirm them as generally applicable conditions.

In conclusion the calculation carried out in the present study suggests that the export of nutrients from the northern Adriatic may actually be counterbalanced by the inflow of nutrient rich waters. This has important implications for nutrient budgets of the Eastern Mediterranean, such as those by Krom et al. (2004, 2010).

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